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Anion exchange polymer coated graphite granule electrodes for improving the performance of anodes in unbuffered microbial fuel cells

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Abstract

In this paper, graphite granule composite electrodes are prepared for microbial fuel cells (MFCs) by coating commercial graphite granules with the mixture of quaternary DABCO polysulfone or Nafion ion exchange polymer and carbon black. The results of electrochemical impedance spectroscopy (EIS) suggest that the addition of carbon black could significantly improve the electrical conductivity of graphite granule anodes. When phosphate buffer solution (PBS) is replaced by NaCl solution, the current densities of the pristine anode, 0.08g Nafion coated anode and 0.16g QDPSU coated anode decrease by 52.6 %, 20.6 % and 10.3 % at -0.2 V (vs. Ag/AgCl), respectively. The solution resistance of ion exchange polymer coated anodes is more stable in comparison with that of pristine anode. After 40 operational days, the performance drop of 0.16 g QDPSU coated anode when switching the solution from PBS to NaCl is still smaller than that of pristine anode. However, 0.08g Nafion coated anode shows the similar performance in NaCl solution to the pristine anode after long term operation. This study reveals that QDPSU anion exchange polymer is more suitable for the anode modification. The QDPSU coated anode promises a great potential for three-dimensional anode based MFCs to treat domestic wastewater.

1. Introduction

Microbial fuel cells (MFCs) can directly convert organic matter in wastewater into electricity. MFCs can be modified for applications of denitrification [1], dye decolorization [2], heavy metal recovery [3] and chemical bio-synthesis [4, 5]. However, because of mild operating conditions and requisite of bacteria catalyzed electrodes, the performance of MFCs is significantly lower than that of conventional fuel cells (e.g., direct alcohol fuel cells). Extensive efforts have been made to improve the cell performance and reduce costs, including improvement of reactor design [6, 7], adoption of three-dimensional electrodes [8], modification of electrodes [9], enrichment of highly specialized microbial communities [10], application of low cost highly active catalysts and biocatalysts [11, 12], and optimization of operating conditions [13].

The anodes of MFCs are attached with microorganisms that facilitate the oxidation of organic matter in wastewater. The anode performance has a great impact on the MFC performance [8]. In comparison to the use of two-dimensional electrodes (e.g. carbon cloth or carbon paper), three-dimensional electrodes have higher surface to volume ratios of up to 6.0×10^{6} m^{2} m^{-3} which increases the attachment of bacteria and improves the anode performance [14]. A number of electrode materials were investigated including graphite granules [15], carbon brush [8], granular activated carbon [16], and nanofiber textile [17]. Lately, a maximum power density of 2420 mW m^{-2} was achieved using a polypyrrole/poly(vinyl alcohol-co-polyethylene) nanofibers/poly(ethylene terephthalate) (PPy/NFs/PET) nanofiber anode [17]. The distance of two-dimensional

anode and cathode can be easily minimized and thus the ionic resistance can be effectively reduced. For a three-dimensional anode based MFC, the distance between the internal parts of the anode to cathode is relatively large. Therefore, the ionic resistance in three-dimensional anode based MFCs becomes a significant factor for limiting the performance of enlarged MFCs when treating domestic wastewater which has a low ionic conductivity (~1 mS cm^{-1}).

Although anode materials have been modified with metal oxides, electron conductive polymers, carbon materials [9, 18-22], there are few reports on modifying anodes for increasing the ionic conductivity. According to our previous report, quaternary DABCO polysulfone (QDPSU) can accelerate OH^- ion transfer of the air cathode resulted in better performance than that of the air cathode using Nafion ionomer [23]. Wang et al. observed the similar phenomenon using an anion exchange resin modified activated carbon (AC) for air cathode MFCs [24].

In this paper, anion exchange polymer is applied on a graphite granules anode (as shown in Figure 1a). The QDPSU anion exchange polymer and cation exchange membrane (Nafion®117) can form a bipolar fuel cell, in which water dissociates into proton and hydroxide ions to participate in anode and cathode reactions (Figure 1b) [25-28]. As a result, the QDPSU coated anode can maintain an anion-rich environment at the vicinity of the three-dimensional anode. Compared to two-dimensional electrodes, the three-dimensional granular graphite electrode provides a large geometric area and significantly increases the polymer loading which helps to reduce the internal resistance of MFCs. Meanwhile, the low cost of graphite granules benefits the scale-up production

of MFCs [29]. In order to reduce the electrical resistance between exoelectrogenic bacteria and graphite granules, fuel cell grade carbon black was introduced together with ion exchange polymers. The Nafion® coated anode was also prepared and characterized as the counterpart of QDPSU coated anodes.

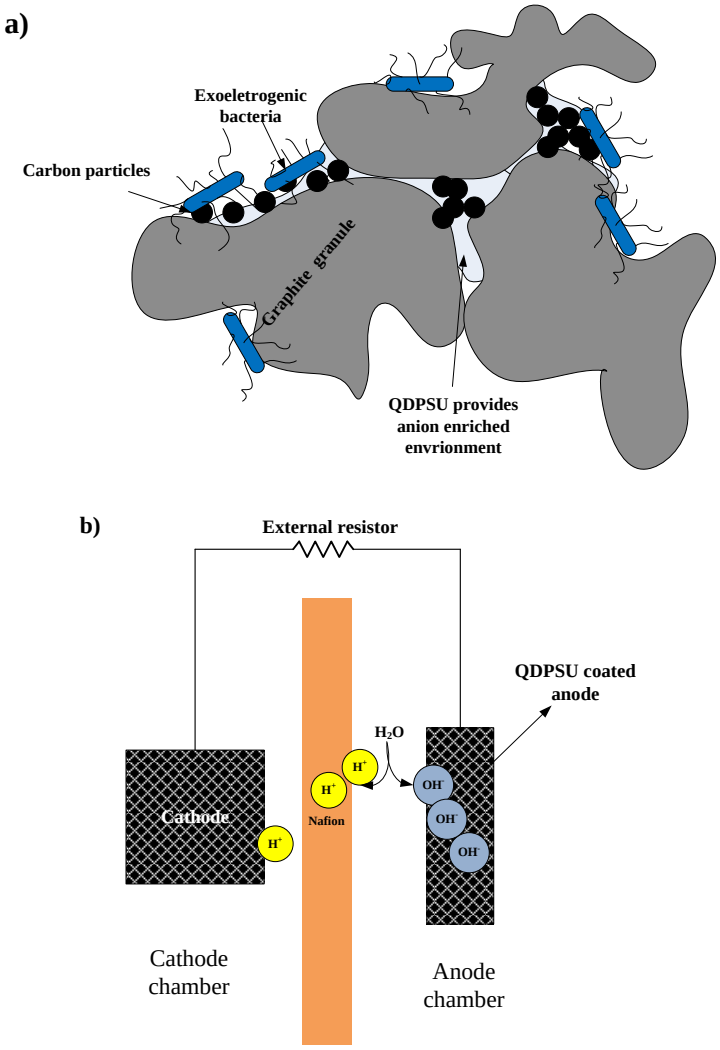


Figure 1 Schematic diagrams of a) anion exchange polymer and carbon black coated graphite granular anode, b) ion transport in a dual-chamber MFC with a QDPSU coated anode.

2. Materials and methods

2.1 Fabrication and characterization of the composite electrodes

Preparation of quaternary DABCO polysulfone was described in previous publications [30, 31]. Since the ion exchange polymers are not electrically conductive, it is necessary to introduce fuel cell grade carbon black for maintaining sufficient electrical contact between the bacteria and the electrode substrate (as shown in Figure 1). Specifically, Vulcan XC-72R carbon black (Cabot, US) and QDPSU (or Nafion) were weighted at a ratio of 4:1 and then dispersed in dimethylacetamide (or ethanol) under ultrasonication for 40 min. The graphite granules (1-2 mm in diameter, Lvlin graphite granules Co., Ltd., China) were pre-washed several times with deionized water to remove contaminations. The titanium mesh cylinders (3.0 cm in diameter and 5.0 cm in height) were used for loading graphite granules. The loaded titanium cylinders were dipped in the mixture of ion exchange polymer and carbon black. Then, the anodes were placed in a furnace at 100 ^{o}C and left overnight to dry.

Morphology of the fabricated anodes was characterized by scanning electron microscopy (SEM, ZEISS-VO18). The surface area of anode materials was measured using the BET method (Micromeritics-ASAP2020, Germany).

The XPS technique was used to analyze the elemental composition of electrodes. XPS spectra were measured with a VG Multilab 2000 by employing AlKα (*hv*=1486.6 eV) irradiation as the photosource, with a primary voltage of 15 kV and an emission current 10 mA. The analysis chamber pressure was 5×10^{-9} Torr during scans.

2.2 MFC configuration and operation

The double-chamber MFCs were constructed by two 250 mL glass bottles with cation exchange membranes (6cm×6cm, Nafion® 117) to separate two electrode chambers, and the liquid volume of two chambers was 170 mL. Carbon paper (Freudenberg FCCT KG, Germany) was cut into 5×5cm electrode and used as the cathode. The anode was incubated from an active, acetate-fed MFC. The medium contained sodium acetate of 1 g L^{-1}, PBS of 50 mM (i.e., 4.09 g L^{-1} Na_2HPO_4, 2.93 g L^{-1} $NaH_2PO4{\cdot}H_2O$, 0.13 g L^{-1} KCl, 0.31 g L^{-1} NH_4Cl), trace minerals of 12.5 mL L^{-1} and vitamins of 5 mL L^{-1}, and the measured ionic conductivity was 6.9 mS cm^{-1}. The unbuffered medium for simulating domestic wastewater contained sodium acetate of 1 g L^{-1}, NaCl of 0.5 g L^{-1}, KCl of 0.13 g L^{-1}, NH_4Cl of 0.31 g L^{-1}, trace minerals of 12.5 mL L^{-1} and vitamins of 5 mL L^{-1}, the ionic conductivity was 2.2 mS cm^{-1}, medium pH was 7.0. The cathode chamber contained 1.67g L^{-1} $K_3Fe(CN)_6$ in 50 mM PBS. The MFC was operated in flow mode by continuously supplying flowing medium and catholyte at a rate of 2 mL min^{-1} under a resistance of 1000 Ω. The hydraulic retention tSime was 8 h. The voltage across the external resistor in the MFC circuit was measured every 20 min using a data acquisition system (2700, Keithley Instrument).

2.3 Electrochemical characterization

The anode performance was measured by conventional three-electrode system using Ag/AgCl (0.197 V vs. standard hydrogen electrode) as the reference electrode and platinum coil (20 cm in length and 0.5 mm in diameter) as the counter electrode.

Polarization curves were recorded using CHI 660E potentiostat (Chenhua instruments, Shanghai, China) with a scan rate of 1 mV s^{-1}. Before recording, the system was pre-scanned for ten cycles. Electrochemical impedance spectroscopy (EIS) tests were conducted over a frequency range from 100 kHz to 0.1 kHz with a sinusoidal perturbation of 10 mV amplitude.

3. Results

3.1 Physical properties of anodes

The pristine graphite granules show a layer-by-layer structure that can create voids for microorganisms to thrive (Figure 2a). Furthermore, ion exchange polymer (QDPSU anion exchange polymer and Nafion) can serve as the binder to hold carbon black on the surface of granules. The electrode was coated with the mixture of ion exchange polymer and carbon black, it can be seen that carbon nanoparticles uniformly cover the surface and meanwhile filled up the micro-voids of graphite granules (Figures 2b-2f).

Large surface area of electrode is desirable for biofilm growth. The surface area of bare electrodes (without bacteria) was characterized using the BET method (in Table 1). The results show that the surface area of electrodes slightly increases with increasing loading of ion exchange polymer and carbon black. It is reasonable to infer that the increased surface area of electrode is attributed to the addition of carbon nanoparticles.

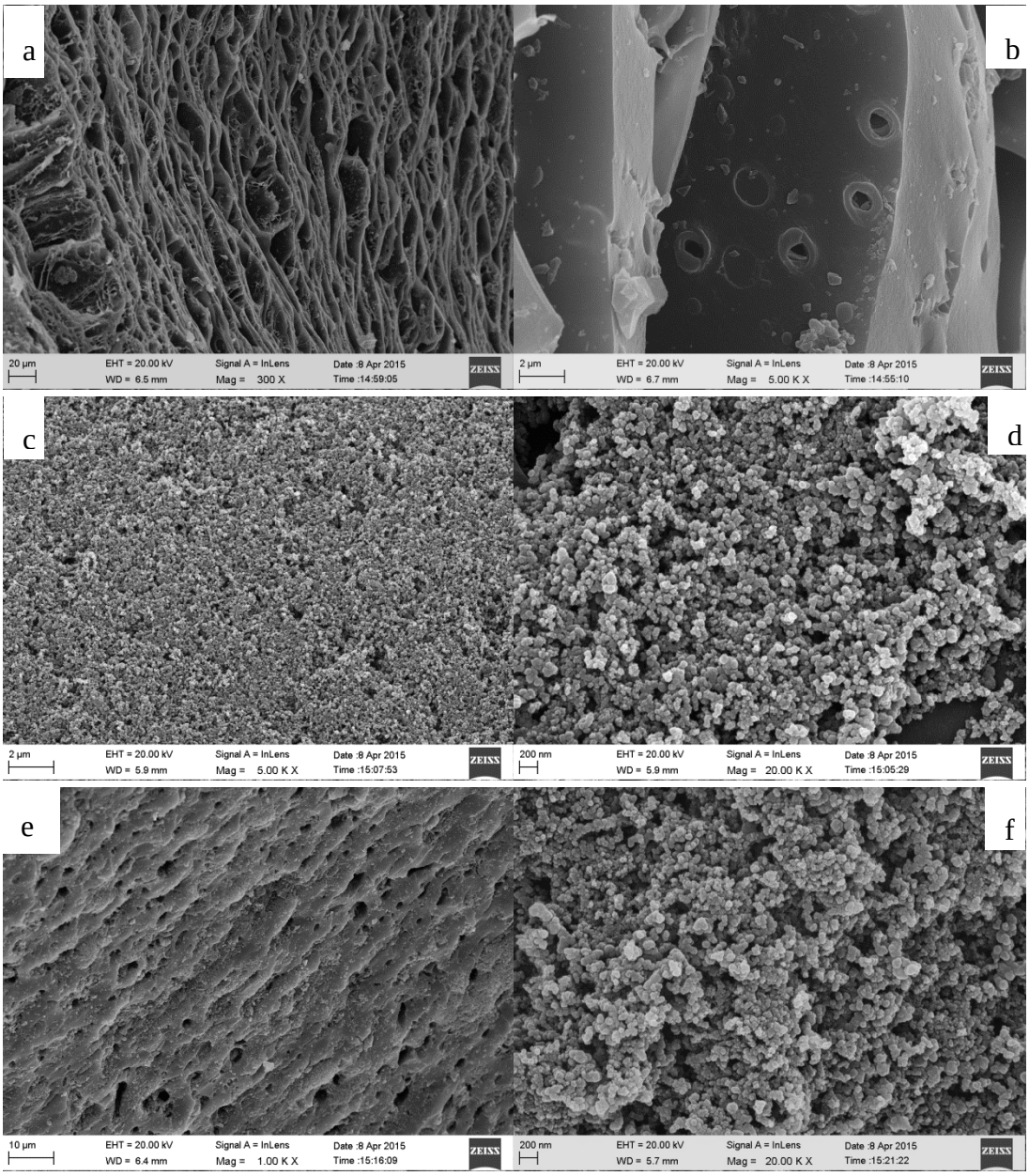


Figure 2 SEM images of bare graphite granules (a and b), Nafion and carbon black coated anode before incubation (c and d), QDPSU and carbon black coated anode before incubation (e and f).

In Figure S1a, the wide-scan XPS survey spectrum of Nafion coated anode reveals F1p and F_{KLL} at 688 eV and 834 eV. All three anodes share the C1s, O1s and O_{KLL} peaks at the same binding energy. The functional group of QDPSU contains nitrogen element and Figure S1b shows the N1s spectra of different anodes. The N1s intensity at 400 eV

in the XPS spectrum of QDPSU coated anode is greater than that of Nafion coated anode and pristine anode. It is suggested that the preparation method of Nafion and QDPSU coated anodes is effective based on the SEM images and XPS analysis.

Table 1 Surface area of the pristine and modified anodes.

Anodes	Carbon black/g	Surface area / m^2g^{-1}
Pristine graphite granule	0.0	514
0.08g*QDPSU	0.32	541
0.16g QDPSU	0.64	556
0.08g Nafion	0.32	534

* Polymer loading

3.2 MFC performance during start-up stage

Figure 3 shows the cell voltage profile of MFCs equipped with the anodes in Table 1 during start-up stage. It can be seen that QDPSU coated and pristine anodes show similar lag period of around 30 h, while the lag period of Nafion coated anode is 20 h longer than that of the others. After the lag period, the cell voltage of MFCs equipped with QDPSU coated anode increases rapidly to a relatively stable value within around 90 h. In contrast, the pristine anode and Nafion coated anode consume 120 h to reach a stable value.

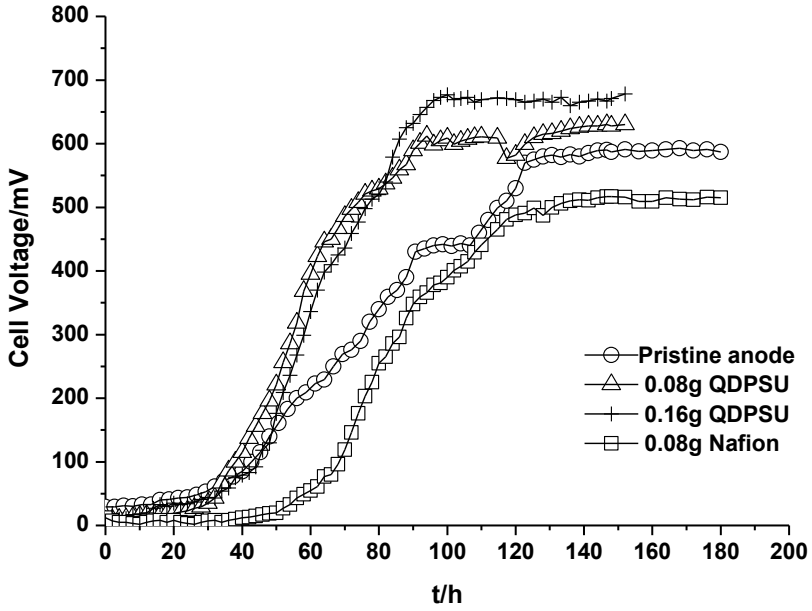


Figure 3 Cell voltage profiles during the start-up stage of MFCs.

3.3 Anode performance in PBS buffered solution

As Figure 4 shows, the onset potential of different anodes is around -400 mV (vs. Ag/AgCl), which is similar to the value from previous reports [9, 20]. The anode polarization curves were recorded within the potential range between open circuit potential (OCP) and 0 V (vs. Ag/AgCl). The potential of the pristine and Nafion coated anodes increase more steeply with the increasing current density compared to that of QDPSU coated anodes. At -0.2 V (vs. Ag/AgCl), the current densities of 0.16 g QDPSU, 0.08 g QDPSU, Pristine anode and Nafion coated anode reach 116 Am^{-3}, 28.5 Am^{-3}, 19.0 Am^{-3} and 18.5 Am^{-3}, respectively. The short circuit current densities of different anodes follow the sequence from high to low as: 0.16 g QDPSU (229 Am^{-3}) > 0.08 g QDPSU (100 Am^{-3}) > 0.08 g Nafion (63.6 Am^{-3}) > pristine anode (33.5 Am^{-3}).

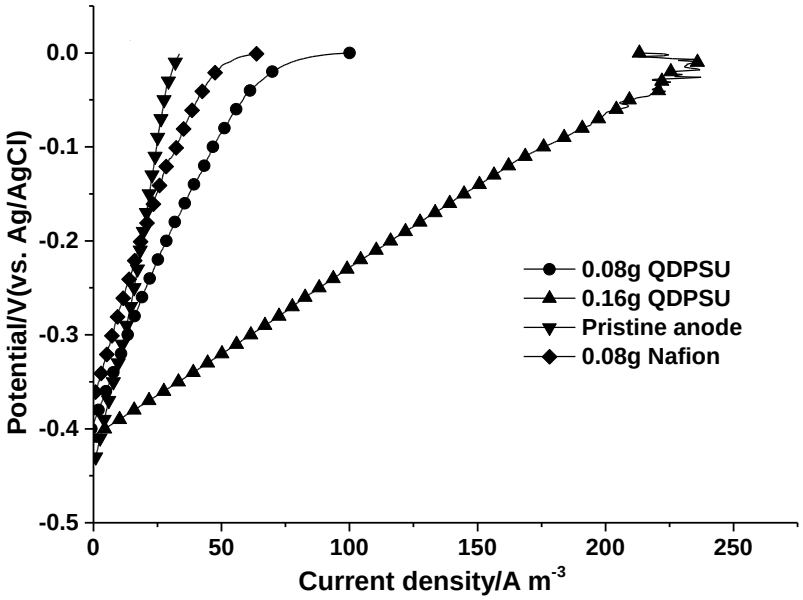


Figure 4 Polarization curves of the anodes in PBS buffered solution.

Electrochemical impedance spectroscopy (EIS) of the anodes was conducted in PBS buffered solution at different external resistances (300 Ω, 10 Ω) and open circuit potential, and the experimental results are shown in Figure 5. Table 2 lists the derived cell circuit data, where R1 represents the impedance of solution (the interception of the arc with the real axis at the highest frequency), R2 is the charge transfer impedance that can be directly determined by the semicircle diameter, and CPE is the constant phase element associated with double layer charge capacitance. As can be seen, R2 shows a significant reduction after coating. This phenomenon can be attributed to the addition of electrically conductive carbon black, which can reduce the resistance of the graphite granule anode.

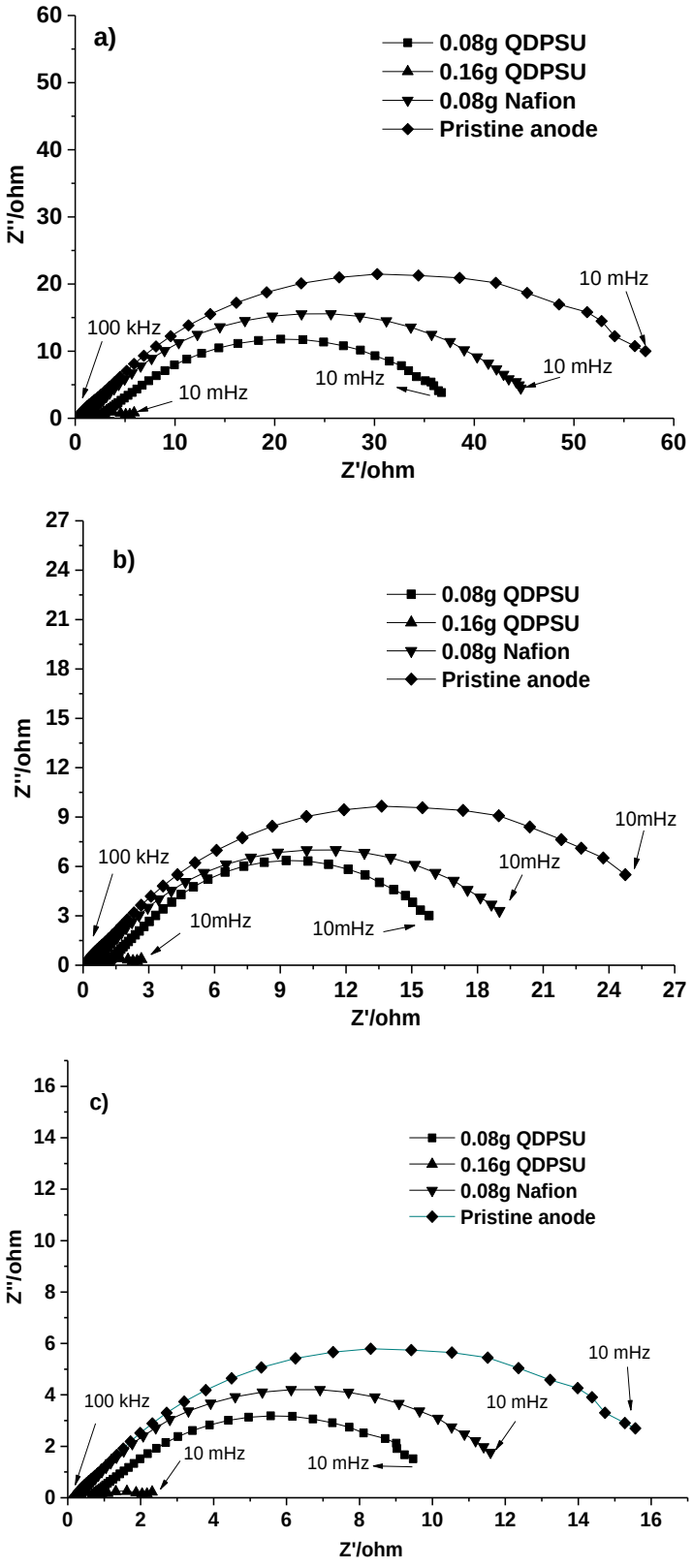


Figure 5 Nyquist plot of different anodes at a) OCP, b) 300 Ω and c) 10 Ω.

Table 2 EIS results of different anodes in PBS buffered solution.

Anodes	State	R_1/Ω	CPE_1-T	CPE_1-P	R_2/Ω
0.08g QDPSU	OCP	1.86	0.013	0.07	38.67
	300Ω	1.85	0.015	0.06	18.56
	10Ω	1.85	0.015	0.07	10.77
0.16g QDPSU	OCP	1.36	0.035	0.51	5.57
	300Ω	1.36	0.032	0.50	2.39
	10Ω	1.36	0.032	0.53	1.43
0.08g Nafion	OCP	0.71	0.014	0.76	48.14
	300Ω	0.74	0.011	0.75	19.10
	10Ω	0.72	0.012	0.75	12.46
Pristine anode	OCP	0.88	0.048	0.74	67.60
	300Ω	0.87	0.045	0.74	30.7
	10Ω	0.87	0.044	0.76	18.33

3.4 Comparison of the performance of anodes in PBS and NaCl solution

Figure 6 shows the polarization curves of the anodes with and without PBS buffer. When the anode solution switched from PBS buffered solution to NaCl solution, the current density decreases by 52.6 %, 20.6 % and 10.3 % at -0.2 V (vs.Ag/AgCl) for pristine, 0.08g Nafion and 0.16g QDPSU coated anode, respectively. EIS of the anodes was also conducted in NaCl solution (Figure 7 and Table 3). In comparison to R1 in PBS buffered solution, the solution resistance of the pristine anode in NaCl solution increases by approximately 40% at different external resistances. In contrast, R1 of Nafion and QDPSU coated anodes is relatively stable.

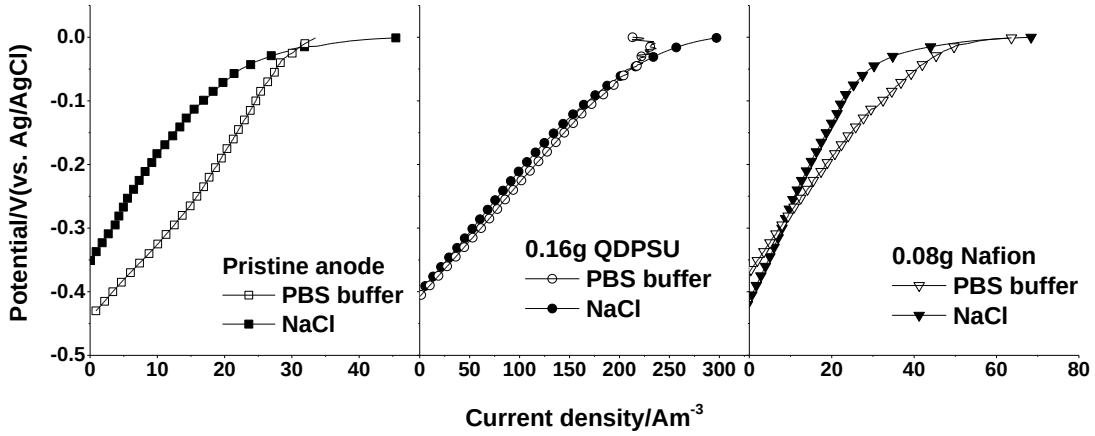
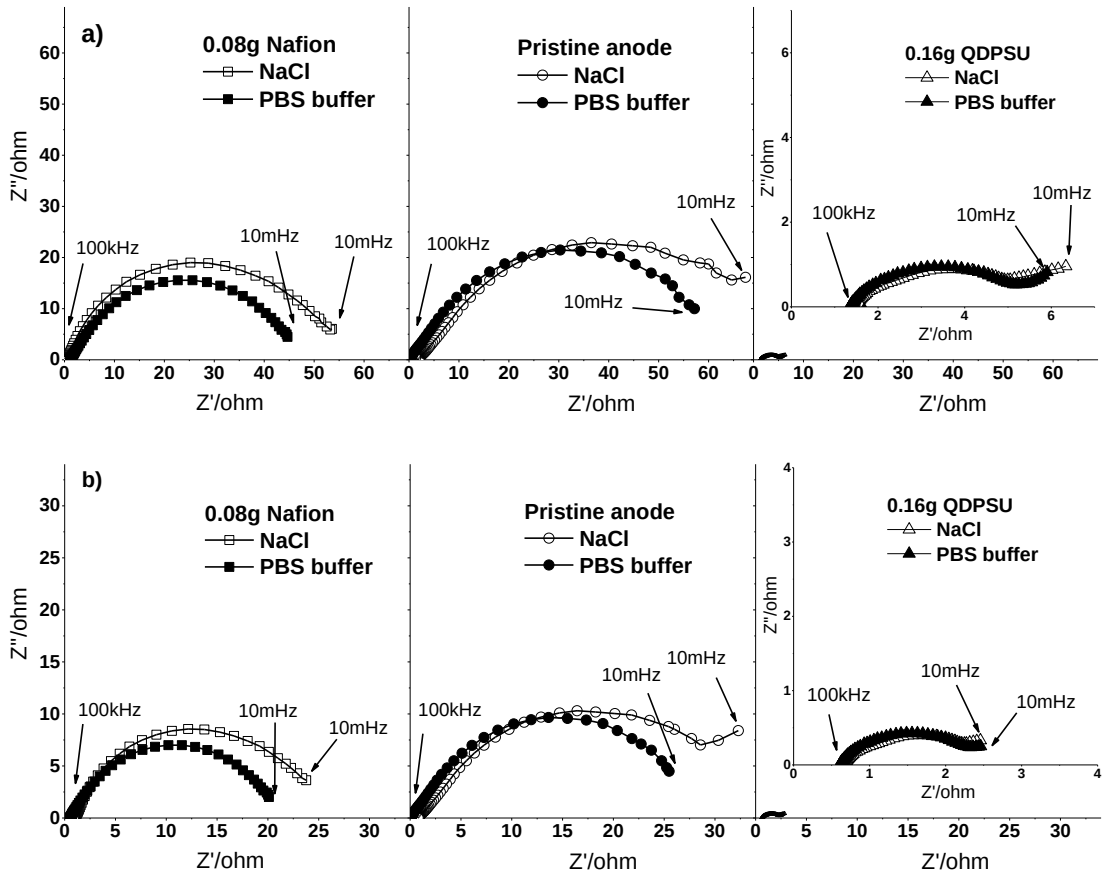


Figure 6 Polarization curves of different anodes in PBS buffer and unbuffered NaCl solution.



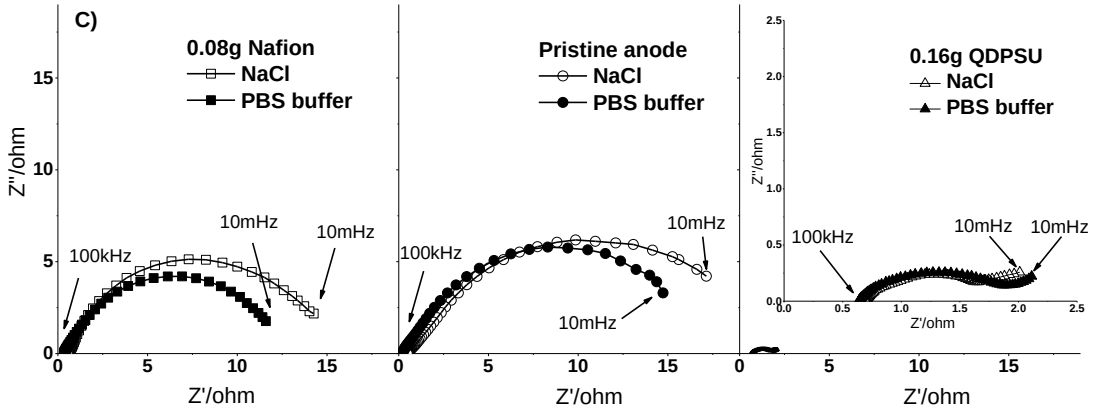


Figure 7 Nyquist plot of the anodes in PBS buffer and NaCl solution at a) OCP, b) 300 Ω and c) 10 Ω.

Table 3 EIS results of the anodes in unbuffered NaCl solution.

Anodes	State	R_1/Ω	CPE_1-T	CPE_1-P	R_2/Ω
0.16g QDPSU	OCP	1.46	0.04	0.51	5.89
	300Ω	1.47	0.04	0.52	2.65
	10Ω	1.45	0.06	0.52	1.49
0.08g Nafion	OCP	0.8	0.027	0.72	59.10
	300Ω	0.8	0.03	0.77	26.6
	10Ω	0.9	0.027	0.75	16.1
Pristine anode	OCP	1.2	0.016	0.66	85.43
	300Ω	1.2	0.014	0.68	38.44
	10Ω	1.3	0.017	0.66	23.06

To investigate the impact of biofilm growth on the anodic performance, the MFCs were operated in PBS solution for up to 40 days under the external resistance of 1000 Ω. Then, the polarization curves of anodes were recorded in NaCl solution (as shown in Figure 8). The performance of pristine anode was slightly improved over time. Both 0.08g Nafion and 0.16g QDPSU coated anodes suffered a performance loss after 20

days and their performances were tend to be stable for another 20 days. After 40 operational days, the current densities of 0.08g Nafion and 0.16g QDPSU coated anodes at -0.2 V (vs.Ag/AgCl) decrease from 14.7 to 11.1 Am^{-3} and 105.7 to 80.1 Am^{-3}, respectively.

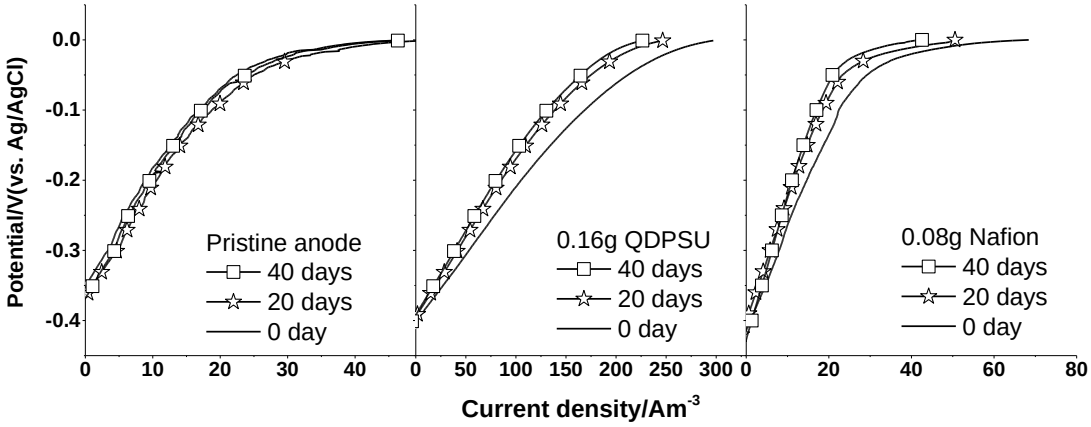


Figure 8 Polarization curves of different anodes in NaCl solution after 20 and 40 operational days.

4. Discussion

Various materials have been reported for anode modification to improve the surface area or electron transfer rate [32]. In this study, the layer-by-layer structure of graphite granules provides a large void space for bacteria growth, but it exhibits a large electrical resistance. Filling the voids inside graphite granules with electronically conductive carbon black significantly increases the contact area for electron transfer (as shown in Figures 2c and 2d), so the electrical resistance of the electrodes can be reduced (R2 in Table 2). By doubling the loading of carbon black, the electrical resistance of 0.16g QDPSU anode is much smaller than that of other composite anodes. This resistance

reduction is attributed to the increased electrical contact between granules. Previous investigations revealed that the current collection dead zone of the packed graphite granule anodes can resulted in large performance loss [29].

In the PBS buffered solution, the QDPSU coated anode exhibits superior performance than the Nafion coated anode with the same loading of polymer and carbon black (Figure 4). It is worthy of noting that the current density at -0.2 V(vs. Ag/AgCl) of Nafion coated anode is 18.5 Am^{-3} which is even smaller that of the pristine anode (19.0 Am^{-3}), regardless of the electrical contact improvement owing to the addition of carbon black. In other words, Nafion ion exchange polymer has a negative impact on the anode performance. The sufonic acid functional group in Nafion and the quaternary ammonium functional group in QDPSU bind to cations (e.g., protons, metal ions) and anions (e.g., hydroxide, chlorine and phosphates) respectively, therefore the pH value at the surface of QDPSU coated anode is higher than that of the surface of Nafion coated anode. It is suggested that the optimal pH range for anodes in MFCs is from 7 to 9 [13, 33, 34]. As illustrated from the cell voltage profile (as shown in Figure 3), the unfavorable pH environment of Nafion coated anode may suppress the biofilm growth during MFC start-up, thus leading to the poor performance.

It is expected that the anode performance may decline in NaCl solution (unbuffered solution) due to the local pH change and the reduced ionic conductivity of solution [24]. The functional groups on Nafion and QDPSU ion exchange polymers can couple with ions that are transported in a “hopping mechanism” [35, 36], which accelerates ionic transfer rate in NaCl solution and reduces the ionic resistance of electrodes. In a

membrane-less air cathode tubular MFC, the distance between the graphite granule anode and the air cathode can be minimized through reactor design. Thus, the ionic resistance of anode accounts for most of the ionic resistance of the whole MFC. Although the performance of QDPSU coated anode degraded after 40 days, the 31% drop on its current density at -0.2 V (vs. Ag/AgCl) after switching the solution from PBS to NaCl is still smaller than that of pristine anode (52.6 %). For the Nafion coated anode, the performance in NaCl solution after 40 days is similar to that of pristine anode. Therefore, the addition of Nafion and carbon black didn't improve the anode performance in both PBS and NaCl solution after long term operation. The experimental results suggest QDPSU anion exchange polymer is more suitable for the anode modification. Furthermore, QDPSU binder simplifies the anode modification (e.g. using metal oxide powder) through the preparation method in this study.

5. Conclusions

In summary, this study demonstrated a novel strategy of improving MFC performance in the absence of PBS by employing ion exchange polymers as solid-state buffer in conjunction with carbon black. Carbon black could fill up the void space of graphite granules and improve the electron conductivity of anodes, while the ion exchange polymer improved the ionic conductivity of anodes. Compared to the Nafion coated anode, the QDPSU anion exchange polymer coated anode showed better performance due to the anion-rich environment. Moreover, the polymer coating could serve as solid-state buffer which don't need constant replenishment. The performance

of QDPSU anode is promising to be used in scale-up MFCs for domestic wastewater treatment.

Acknowledgements

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